Summary of commercially available pheromones of common stored-product beetles

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Abstract

1. Introduction

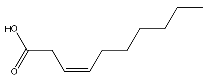
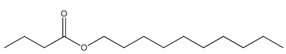
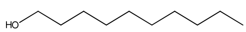
Since the explosion of pheromone identification and synthetic production of the 1960's, pheromone utilization has become a valuable technique for monitoring and control of insect infestations (Cork, 2004) Pheromones are collectively grouped into one family of specific chemical signals designated as semiochemicals. Specific pheromones in this category are synthetically created, placed in traps that are in turn used for population tracking, stages of development and mating disruption of common stored-product pest beetles. These insects have the dexterity to infest processed foods, whole grains such as barley, rye, corn, oat and rice. Trapping and monitoring through pheromone usage can assist in reducing the amount of insecticide used by pest-control managers, only spraying when insects surpass certain levels or when they enter a vulnerable stage.

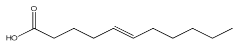
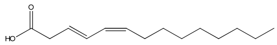
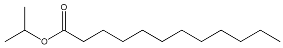
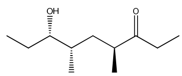
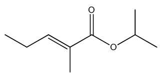
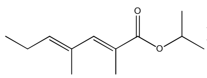
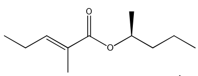
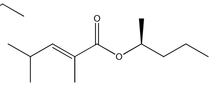
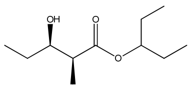
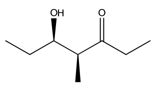
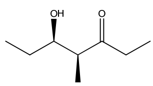
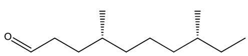
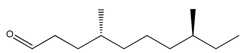
Many stored-product pest beetles produce pheromones that can be classified as long-chain carbon compounds, predominately consisting of acids, aldehydes, acetates and esters. Many of these pheromones are unsaturated and consist of one or more double bonds that can be oriented into an E or Z conformation creating one or more isomers. Pheromones produced by stored-product beetles are generally more complex when compared with pheromones produced by stored-product moths. As a result of this complexity, stored-product beetle pheromones contain a degree of chirality creating additional isomers. The chemistry used for producing these compounds is more involved but can be easily reproduced and contains highly stable intermediates leading to the commercial availability of these particular pheromones.

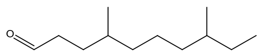
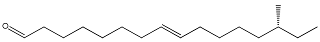
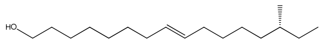
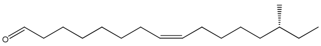
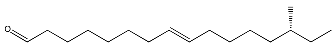
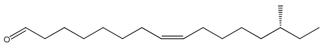
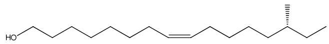
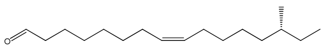
2. Commercially available pheomones for stored-product

The majority of pheromones range anywhere from 7-18 carbons in length producing carbon-chained compounds. Pheromones vary by functional group (i.e., acid, aldehyde, acetate, ester), double bond position and the configuration of the double bond (E or Z). Some of these pheromones are also branched containing methyl groups at various positions on the compound. These methyl groups create chirality in the compound depending upon how they are oriented on the molecule (R or S configuration). These factors are attractant determining for a variety of different beetles. Small changes in double bond placement and orientation of double bond or methyl group substituents may prevent attraction. The same holds true for alterations of functional groups. Through the use of organic syntheses, coupling of smaller organic compounds and the manipulation of long chain carbon compounds, these particular beetle pheromones can be made commercially available.

Table 1 Commercially available pheromones for common stored-product pest beetles.

Scientific Name / Common Name	Pheromone Structure	Pheromone Name / Ratio
Anthrenus flavipes LeConte Furniture carpet beetle		(Z)-3-Decenoic Acid
Anthrenus sarnicus Mroczkowski Guernsey carpet beetle	 	Decy butyrate (1) Decan-1-ol (1)

Scientific Name / Common Name	Pheromone Structure	Pheromone Name / Ratio
Anthrenus verbasci(L.) Varied carpet beetle		(E)-5-Undecenoic acid
Attagenus unicolor (Brahm) Black carpet beetle		(E,Z)-Tetradecadienoic acid
Dermestes maculatus De Geer Hide beetle		11 isopropyl ketones: (Z)-5-dodecenoate, (Z)-7-dodecenoate, (Z)-9-dodecenoate, tetradecanoate, dodecanoate, (Z)-5-tetradecenoate, (Z)-9-tetradecenoate, hexadecanoate, (Z)-9-hexadecenoate, oleate
Lasioderma serricone(F.) Cigarette beetle		(4S,6S,7S)-7-hydroxy-4,6-dimethylnonan-3-one
Prostephanus truncatus (Horn) Larger grain borer	 	1-Methylethyl (E)-2-methyl-2-pentenoate (2) 1-methylethyl (E,E)-2,4-dimethyl-2,4-heptadienoate (1)
Rhyzopertha dominica (F.) Lesser grain borer	 	(S)-1-Methylbutyl (E)-2-methyl-2-pentenoate (S)-1-Methylbutyl (E)-2,4-dimethyl-2-pentenoate
Sitophilus granarius (L.) Granary weevil		(2S,3R)-1-Ethylpropyl 2-methyl-3-hydroxypentanoate
Sitophilus oryzae (L.) Rice weevil		(4S,5R)-5-Hydroxy-4-methylheptan-3-one
Sitophilus zeamais Motschulsky Maize weevil		(4S,5R)-5-Hydroxy-4-methylheptan-3-one
Tribolium castaneum (Herbst) Red flour beetle	 	(4R,8R)-4,8-Dimethyldecanal (8) (4R,8S)-4,8-Dimethyldecanal (2)

Scientific Name / Common Name	Pheromone Structure	Pheromone Name / Ratio
Tribolium confusum Jaquelin du Val Confused flour beetle		4,8-Dimethyldecanal
Trogoderma glabrum Everts Glabrous cabinet beetle	 	(R)-(E)-14-Methyl-8-hexadecenal (R)-(E)-14-Methyl-8-hexadecen-1-ol
Trogoderma granarium Everts Khapra beetle	 	(R)-(Z)-14-Methyl-8-hexadecenal (R)-(E)-14-Methyl-8-hexadecenal
Trogoderma inclusum (LeConte) Larger cabinet beetle	 	(R)-(Z)-14-Methyl-8-hexadecenal (R)-(Z)-14-Methyl-8-hexadecen-1-ol
Trogoderma variable BallionWarehouse beetle		(R)-(Z)-14-Methyl-8-hexadecenal

In some instances, the same pheromone has the ability to attract more than one species of beetle. This holds true for the warehouse, larger cabinet, and khapra beetles. In this example, a 16-carbon aldehyde with a Z conformation of the double bond is used to attract all three. The glabrous cabinet beetle is attracted by essentially the same compound only the double bond having an E configuration. Variations to this pheromone's functional group or E or Z configuration can be blended with the original pheromone to capture one particular beetle exclusively. The ketone, (4S,5R)-5-Hydroxy-4-methylheptan-3-one, attracts both the rice and maize weevil containing a hydroxyl group in the R configuration and a methyl substituent in the S configuration. In a majority of the stored-product beetle pheromones, attractants are strictly isomeric specific. Variations in double bonds, substituents, and functional groups will greatly reduce the effectiveness of insect response to the synthetically created pheromone in most cases.

Most pheromone syntheses start with two smaller compounds to be coupled together to form these larger carbon-chained compounds. Other syntheses can utilize ring opening chemistry which converts a cyclic compound into a straight chain compound with or without methyl or hydroxyl substituents depending upon the structure of the original compound. After an acceptable synthesis is discovered for one particular pheromone, similar pheromones can be created in the same manner only adjusting the length or overall structure of the starting compounds. Functional group, double bond configuration and orientation (E,Z), and the more challenging R or S configurations of methyl or hydroxyl groups need to be considered when choosing starting materials.

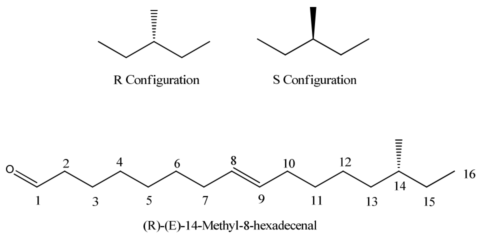


Figure 1 Methyl group R and S configurations and double bond placement of (R)-(E)-14-Methyl-8-hexadecenal.

For the capture of certain pest beetles, two closely related pheromones are used. Most of these multi-compound pheromones are used in very specific ratios, some having only one component making up significantly less of the overall solution. Research has shown that specific ratios of closely related compounds have the ability to increase effectiveness of captures. Some attractants combine more than just a couple of pheromones; the hide beetle attractant contains 11 closely related ketones varying in carbon chain length.

The stored-product beetle pheromones presented are commercially available due to three factors:

1. The starting materials for synthesis are available and inexpensive: It would not make sense to start a multi-step synthesis with costly starting materials. The overall amount of money spent producing the final desired product will skyrocket when the cost of the smaller components used for coupling increase.
2. Ease of organic reactions and reproducibility is acquired: The chemistry preformed results in high yields and high purity. The complexity of the chemistry needed to produce a particular pheromone is low.
3. Syntheses contain highly stable intermediates**:** In multi-step syntheses the product between sequential reactions must be stable and not degrade before moving on to the next reaction.

Other pheromones that don't reach these criteria more than likely are pheromones consisting of more complex compounds and require more complicated chemistry to produce. Any organic synthesis of a stored-product beetle pheromone that meet the criteria above can be used in formulated lures bought from commercial suppliers.

Table 2 Commercial suppliers of formulated lures for stored-product pests

Cooper Mill Ltd., R. R. 3 Madoc, ON, Canada
Fuji Flavor, 358 Midorigaoka, Hamura-Shi, Tokyo, Japan.
Hercon Environmental, Emigsville, PA , USA.
ISCA Technologies, 1230 Spring St., Riverside, CA, USA
Insects Limited Inc., 16950 Westfield Park Road, Westfield, IN, USA.
Russell Fine Chemicals, Unit 68, Third Ave., Deside Industrial Park East, Deeside, Flintshire UK
Suterra Corporate, 20950 NE Talus Place, Bend, OR, USA
Trece Inc., P.O. Box 6278, 1143 Madison Lane, Salinas, CA, USA.

References

Cork, A., 2004. Pheromone Manual. Natural Resources Institute, Chatham Maritime , UK.

Mayer, M.S., McLaughlin, J.R., 1991. Handbook of insect pheromones and sex attractants. CRC Press, Inc., Boca Raton, FL, USA.